Message

From: Barlet, Nathan [barlet.nathan@epa.gov]
Sent: 5/6/2020 12:47:46 PM
To: Strynar, Mark [Strynar.Mark@epa.gov]; McCord, James [mccord.james@epa.gov]
CC: Washington, John [Washington.John@epa.gov]
Subject: RE: PFAS Question - PFECA synthesis & Industrial Waste Streams

Good Morning Mark and James,

Thank you again for sharing! This does help elucidate the distinct synthesis processes.

All the best!

Nate

Nathan T. Barlet
Environmental Engineer
Technology Integration & Information Branch
U.S. EPA | Office of Superfund Remediation & Technology Innovation
2777 Crystal Drive | Arlington, VA 22202
Office: (703) 603-8761
Mobi Ex. 6 Personal Privacy (PP)

From: Strynar, Mark <Strynar.Mark@epa.gov>
Sent: Monday, May 4, 2020 11:44 AM
To: McCord, James <mccord.james@epa.gov>; Barlet, Nathan <barlet.nathan@epa.gov>
Cc: Washington, John <Washington.John@epa.gov>
Subject: Re: PFAS Question - PFECA synthesis & Industrial Waste Streams

Everything I have is for synthesis (see attached) nothing on dealing with the waste stream.

Mark

Dr. Mark Strynar
US EPA/ORD/CEMM
strynar.mark@epa.gov
(office) 919-541-3706
(mobile) Ex. 6 Personal Privacy (PP)

From: McCord, James <mccord.james@epa.gov>
Sent: Monday, May 4, 2020 11:40 AM
To: Barlet, Nathan <barlet.nathan@epa.gov>; Strynar, Mark <Strynar.Mark@epa.gov>
Cc: Washington, John <Washington.John@epa.gov>
Subject: RE: PFAS Question - PFECA synthesis & Industrial Waste Streams

Nathan,

You are definitely correct that there are a large number of synthesis pathways and product lines; everyone is doing their own sort of chemistry for fluoroethers and some of the emergent PFAS. I do not have any thorough references for the possible contents of fluoro-ether waste streams in general. Mark has an outline for at least the Chemours Fayetville site that we reverse engineered from our monitoring, and I have some patent and early synthesis literature for specific chemical products that we've been looking at. It's definitely not an exhaustive examination of the literature but would those be helpful?

--
James McCord

From: Barlet, Nathan <barlet.nathan@epa.gov>
Sent: Friday, May 1, 2020 9:30 AM
To: McCord, James <mccord.james@epa.gov>; Strynar, Mark <Strynar.Mark@epa.gov>
Cc: Washington, John <Washington.John@epa.gov>
Subject: RE: PFAS Question - PFECA synthesis & Industrial Waste Streams

Mark and James,

Thank you for sharing your insights!

The Buck et al (2011) paper + supplemental info and the OECD updated list of PFAS both seem to treat FT-based substances and poly- and perfluoro ether based substances as products of distinct processes. There also seems to be multiple synthesis pathways for PFPEs which includes the polymerization of HFPO, as well as UV-initiated copolymerization of TFE with O2, and or photo-polymerization of HFP instead of/or with TFE, resulting in different structures.

Do either of you have any references you would recommend that discuss the release of initial product and thermal byproducts in gas/liquid/solid phase waste streams of poly- and perfluoro ether synthesis and their subsequent breakdown?

Thank you again for your assistance, enjoy your weekend!

Nate

Nathan T. Barlet
Environmental Engineer
Technology Integration & Information Branch
U.S. EPA | Office of Superfund Remediation & Technology Innovation
2777 Crystal Drive | Arlington, VA 22202
Office: (703) 603-8761
Mobil Ex. 6 Personal Privacy (PP)

From: McCord, James <mccord.james@epa.gov>
Sent: Thursday, April 30, 2020 3:06 PM
To: Strynar, Mark <Strynar.Mark@epa.gov>; Barlet, Nathan <barlet.nathan@epa.gov>
Cc: Washington, John <Washington.John@epa.gov>
Subject: RE: PFAS Question - PFECA synthesis & Industrial Waste Streams

Nathan,

One thing to note about the GenX and PFECA distinction. We found in Fayetville that Chemours was producing GenX intentionally for use as a polymer processing aid on a "closed loop" system, but we found a large number of PFECA compounds, including GenX, as byproducts of polymer production. It's possible the main GenX production is very different from what we observe in the polymerization process and its waste products.

As Mark said the PFECAs are HFPO polymers, I don't think it is strict telomerization due to the mechanism of the HFPO ring opening (which would be either a radical or anionic ring opening polymerization), but that's a distinction that likely matters to industrial and inorganic chemists and not so much to me. In either case, it's still an aprotic polymerization catalyzed by metal salts.

The waste streams from the HFPO polymerization processes are more closely similar to ECF products in terms of their isomeric character, we see lots of closely related structures with identical molecular weights but minor variations in retention time and MS/MS structures. We do not actually have a clear picture of the sources of all the isomers but there are definitely linear vs. branched monomer unit incorporations in some locations. The preferred form is a slightly branched structure (monomers connect on the oxygen and middle carbon of HFPO) based on our communications with Chemours at least. We also observe copolymerization at locations where they are making multiple types of fluoropolymers, so you can have a heterodimer between, for example the sulfonated Nafion Precurosor Monomer and HFPO at the Fayetville Chemours plant or HFPO and fluoroethene/fluoroproylene in WV where they are making polyfluoroalkoxyalkane.

Something else to mention is that the initial products are typically acyl or sulfonyl fluorides and they hydrolize to carboxylic and sulfonic acids. We expect a lot of the gas waste streams to be the acyl-/sulfonyl compounds and they hydrolize atmospherically, while obviously the liquid and solid streams are going to be the acid forms. There are also probably gas phase productions of the thermal breakdown products, which are hydrides/polyfluorinated compounds and probably much more susceptible to certain kinds of breakdown because they have an attackable hydrogen.

Those are just some of my thoughts.

--
James McCord

From: Strynar, Mark <Strynar.Mark@epa.gov>
Sent: Thursday, April 30, 2020 1:46 PM
To: Barlet, Nathan <barlet.nathan@epa.gov>
Cc: Washington, John <Washington.John@epa.gov>; McCord, James <mccord.james@epa.gov>
Subject: Re: PFAS Question - PFECA synthesis & Industrial Waste Streams

Nathan,

GenX and related PFECAs are made from the polymerization of HFPO (hexafluoropropylene oxide) which can results and short 2 subunits oligomers (HFPO-DA dimer acid - GenX) and larger polymers with many subunits (Krytox). It is for sure different from ECF. However I am not sure if this would be considered different from telomerization as is used to produce fluorotelomer alcohols. The book by Erik Kissa (https://www.amazon.com/Fluorinated-Surfactants-Repellents-Surfactant-Science/dp/082470472X) may give some insight.

The main difference in the waste stream would be lots of polyfluoro ether substances, rather than simply perfluorinated chains. The oxygen linkage should be a weak spot for destruction.

I am attaching two European patent applications for the polymerization of HFPO. Also perhaps James can chime in on this.

Mark

Dr. Mark Strynar
US EPA/ORD/CEMM
strynar.mark@epa.gov
(office) 919-541-3706
(mobile) Ex. 6 Personal Privacy (PP)

From: Barlet, Nathan <barlet.nathan@epa.gov>
Sent: Thursday, April 30, 2020 11:43 AM
To: Strynar, Mark <Strynar.Mark@epa.gov>
Cc: Washington, John <Washington.John@epa.gov>
Subject: PFAS Question - PFECA synthesis & Industrial Waste Streams

Hello Mark,

I hope all is well. John Washington recommended that I reach out to you for some questions I have regarding the synthesis of PFECAs. I am currently assisting an EPA workgroup in the development of guidance for destruction and disposal of PFAS-containing wastes. Specifically, I am working on the discussion of solid, liquid, and gas waste streams generated by manufacturers and industrial users of PFAS-containing materials. I had a question regarding primary synthesis methods for PFAS. Many reports suggest that the two primary large-scale production methods include ECF and telomerization. Is the synthesis of PFECAs such as GenX considered a separate process distinct from either ECF or telomerization? Could you please provide any insight into the PFAS-containing waste streams generated by these processes, and do they differ in any way? Thank you for your time!

All the best,

Nate

Nathan T. Barlet
Environmental Engineer
Technology Integration & Information Branch
U.S. EPA | Office of Superfund Remediation & Technology Innovation
2777 Crystal Drive | Arlington, VA 22202
Office: (703) 603-8761
Mobile Ex. 6 Personal Privacy (PP)